

## SHORT RESIDENCE TIME COAL LIQUEFACTION

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### INTRODUCTION

Based on prior work reported by the Mobil Research and Development Corporation, a two-step coal liquefaction process seems to have potential for savings on hydrogen usage compared to conventional solvent-refined coal (SRC) technology.<sup>(1)</sup> The first step consists of a short contact time, relatively low temperature, low pressure reaction of coal with a coal derived solvent in the absence of molecular hydrogen. This is followed by a short contact time, high pressure and temperature reaction of the products in the presence of molecular hydrogen. The purpose of the first step is primarily to dissolve the coal. After removal of unreacted coal and mineral matter, the second step is carried out to reduce the sulfur level of the product and to regenerate the solvent. Decreased hydrogen consumption is expected to result from the short contact times and the removal of mineral matter and sulfur before the addition of molecular hydrogen.

### EXPERIMENTAL

The apparatus constructed to carry out the experiments consisted of a 1-liter, stirred autoclave (AC1) used to preheat the solvent-coal slurry connected to a 2-liter, stirred autoclave (AC2) equipped with an internal heating coil to bring the solvent-coal slurry rapidly to a constant reaction temperature. The apparatus was later modified by the addition of a third autoclave (AC3) to act as a quench vessel. This allowed direct determination of the material lost in each transfer step and an unambiguous determination of the product yield. Two of the experiments required a high-pressure hydrogen atmosphere. A thermostatted hydrogen cylinder was added with a precise pressure gauge to determine the hydrogen gas balance in these experiments. A drawing of the 3-autoclave apparatus is shown in Figure 1. The slurry transfer lines were heat-traced 1/4-inch tubes equipped with quick-opening valves which could be manually operated through a safety barrier. AC2 was equipped with a thermocouple in the autoclave body as well as in the solution for precise temperature control. During venting, the gas passed through a trap to condense liquids, a gas sample port, an H<sub>2</sub>S scrubber, and a wet test meter to measure H<sub>2</sub>S free gas volume.

The experimental procedure consisted of preheating the coal-solvent slurry to 250 C in AC1 while AC2 was heated empty to slightly higher than the desired temperature. The slurry was transferred to AC2 and the internal heater was used to bring the slurry rapidly to constant reaction temperature. Typically, heatup required  $3.4 \pm 0.6$  min and the temperature remained constant within  $\pm 1.0$  degrees during the reaction period. Small variations in heatup time did not affect the reaction since most of the heatup time was spent below 415 C where the reaction was slow. After the reaction was complete the slurry was transferred back to AC1 or to AC3 where it was quenched to 250 C using an internal cooling coil. After the gases were vented the slurry was transferred to a heated filter and filtered at 250 C.

The product workup consisted of continuously extracting the filter cake with tetrahydrofuran (THF) and combining the proper proportions of THF and filtrate to make up a sample for distillation. The procedure was later modified to include routine extraction of the THF extracted filter cake with pyridine and the inclusion of the pyridine extract in the liquid products. The entire hot filtrate-THF and pyridine extract was distilled to eliminate any questions regarding the use of

a representative sample for distillation. Distillation cuts were made to give the following fractions, THF (b.p. <100 C), light oil (b.p. 100-232 C), solvent (b.p. 232-482 C), and SRC (distillation residue b.p. >482 C).

# MATERIALS

The coal used for experiments 1-28 was supplied from the Wilsonville SRC pilot plant, Sample No. 15793. It was a blend of West Kentucky 9 and 14 seam coal from the Colonial Mine of the Pittsburgh and Midway Coal Company. The coal used in experiments 29-37 was similar but contained 0.39 weight percent more organic sulfur than the first coal. Analyses of both coals are shown in Table 1.

TABLE 1. ANALYSES OF STARTING COALS  
(As-Received Basis)

| Coal Type                       | West Kentucky 9/14           | West Kentucky 9/14                  |
|---------------------------------|------------------------------|-------------------------------------|
| Source                          | Colonial Mine <sup>(a)</sup> | Pittsburgh &<br>Midway Coal Company |
| <u>Proximate Analysis, wt %</u> |                              |                                     |
| Moisture                        | 5.72                         | 2.71                                |
| Ash                             | 12.71                        | 8.90                                |
| Volatile matter                 | 34.7                         | 36.9                                |
| Fixed carbon                    | 47.5                         | 51.49                               |
| <u>Ultimate Analysis, wt %</u>  |                              |                                     |
| Carbon                          | 66.0                         | 70.0                                |
| Hydrogen                        | 4.7                          | 4.8                                 |
| Nitrogen                        | 1.3                          | 2.4                                 |
| Sulfur                          | 3.75                         | 3.16                                |
| Oxygen                          | 12.2                         | 10.74                               |
| <u>Sulfur Types, wt %</u>       |                              |                                     |
| Total                           | 3.77                         | 3.16                                |
| Pyritic                         | 1.96                         | 1.30                                |
| Sulfate                         | 0.64, 0.56                   | 0.31                                |
| Sulfide                         | 0.01                         | --                                  |
| Organic (by difference)         | 1.16                         | 1.55                                |

(a) Source of coal used at Wilsonville, SRC Quarterly Report #1,  
June 25, 1976, p 2.

The solvent used for experiments 1-28 was recycle solvent obtained from the Wilsonville SRC pilot plant, Sample No. 20232. An analysis and distillation data for the solvent are shown in Table 2. The solvent contained 5 percent of material boiling below 232 C, the cutoff point between light oil and SRC in the product distillation and 4-5 percent of material boiling above 482 C, the cutoff point between solvent and SRC.

A blend of Wilsonville recycle solvent (75 weight percent), and 1,2,3,4-tetrahydronaphthalene, J. T. Baker Company Practical Grade (25 weight percent), was prepared for use as the solvent in experiments 29-37. Analyses and distillation data are also given in Table 2. Tetralin boils below 232 C and was collected in the light oil distillation fraction during product workup.

TABLE 2. SOLVENT ANALYSES

| <u>Ultimate Analysis, wt %<br/>as received</u> | <u>Wilsonville Recycle Solvent</u> |  | <u>3:1 Wilsonville Recycle<br/>Solvent-Tetralin</u> |       |
|--|------------------------------------|--|---|-------|
|  |                                    |  |   |       |
| Moisture (benzene azeotrope)                   |                                    |  |   | Trace |
| Ash  | <0.01                              |  |   | 0.10  |
| Carbon   | 87.8                               |  |   | 87.9  |
| Hydrogen                                       | 7.8                                |  |   | 8.3   |
| Nitrogen                                       | 0.7                                |  |   | 0.6   |
| Sulfur   | 0.27                               |  |   | 0.21  |
| Oxygen (by difference)                         | 3.42                               |  |   | 2.89  |
| H/C  | 1.07                               |  |   | 1.13  |

| <u>Corrected<br/>Temp, C</u> | <u>Cumulative<br/>Volume Distilled<br/>% of Sample</u> | <u>Corrected<br/>Temp, C</u> | <u>Cumulative<br/>Volume Distilled<br/>% of Sample</u> |
|------------------------------|--|------------------------------|--|
| 216                          | IBP  | 201                          | IBP  |
| 248                          | 10   | 210                          | 4  |
| 253                          | 20   | 214                          | 17   |
| 267                          | 30   | 225                          | 28   |
| 281                          | 40   | 236                          | 36   |
| 299                          | 50   | 260                          | 47   |
| 319                          | 60   | 310                          | 68   |
| 356                          | 70   | 340                          | 76   |
| 406                          | 80   | 390                          | 86   |
| 431                          | 90   | 430                          | 90   |
| 444                          | 95.5   | 481                          | 94.5   |
| >444                         | 4.5 wt % residue                                       | >481                         | 4.1 wt % residue                                       |

### RESULTS AND DISCUSSION

Four variables were studied in the first part of the experimental program which examined the first step of the proposed two-step process. The variables were reaction temperature (413-454 C) solvent to coal ratio (2:1 and 3:1), residence time, (0-5 minutes), and pressure (300-1800 psi). Recycle solvent from the Wilsonville SRC pilot plant was used in all of these experiments. Later, molecular hydrogen and recycle solvent containing 25 weight percent tetralin were used in four experiments, all at 441 C for 2 minutes. These experiments were designed to simulate the second step, where hydrogenated solvent and molecular hydrogen would be used to lower the sulfur content of the product.

#### THF Conversion

Tetrahydrofuran (THF) conversion was calculated from the difference between the initial and the final solubilities of the total coal-solvent slurry in THF. THF conversions were calculated on an MAF coal basis and adjusted for the coal not recovered from the autoclaves. The filter cake resulting from filtration of the product at 250 C was continuously extracted with THF for up to three days. The THF soluble conversion figures may be too high however, since hot recycle solvent is probably a better solvent for coal liquids than THF and may have dissolved some material in the hot filtration which would be insoluble in THF.

Figure 2 shows THF conversion plotted as a function of reaction time and temperature at 3:1 solvent/coal ratio. The THF solubles appear to be formed as unstable intermediates in the total reaction sequence. The low molecular weight THF solubles may be able to combine in the absence of hydrogen to form higher molecular weight materials which are insoluble in THF. At 413 C, THF solubles increase ly between 0 and 2 minutes and seem to be only slightly unstable. At 429 C, most

of the THF solubles are produced during the heatup period. The formation of THF solubles is over by the end of the heatup period and decomposition is slowly taking place after "zero" reaction time at 441 C, and at 454 C the production of THF solubles is over before the heatup period is completed and the thermal decomposition reaction is more rapid than at 441 C.

Increasing the solvent to coal ratio might be expected to have the effect of stabilizing the THF soluble materials by making available more hydrogen from the solvent. However the changes in THF conversion as a function of solvent to coal ratio at 1 minute residence time and 427-441 C are relatively small. THF soluble conversion is increased by the presence of both molecular hydrogen in the gas phase and tetralin added to the solvent.

Solubilities of the products in THF followed by pyridine were determined for some of the experiments. The conversions to pyridine solubles averaged 1.6 weight percent more than the conversions to THF solubles.

#### SRC Yields

SRC yield is defined as the material which is soluble in the hot filtrate plus the material in the filter cake which is soluble in THF with a boiling point above 482 C. All of the SRC yields have been calculated on an MAF coal and MAF SRC basis. The yields of SRC would normally be smaller than the THF soluble conversions were it not for the presence of the solvent. Components of the solvent reported to the SRC fraction either by reacting with the SRC or by polymerizing to higher molecular weight materials which appear in the SRC distillation fraction. In addition, 4-5 weight percent of the starting solvent boiled above 482 C and was included in the SRC during distillation.

Figure 3 is a plot of SRC yield versus time and temperature at 3:1 solvent to coal ratio. SRC yields are shown to decrease at 413 C and 427 C and to increase at 441 C and possibly 454 C as a function of increasing reaction time at temperature. One explanation for these results lies in the thermal instability of the solvent. The product of the interaction of SRC with solvent may decompose at 413 and 427 C releasing solvent molecular weight material while at 441-454 C the solvent may polymerize to heavier molecular weight products which distill with the SRC fraction.

There was a decrease in SRC yield when tetralin was added to the solvent but a slight increase when an overpressure of hydrogen was used. The decrease with added tetralin was probably due to the fact that there was less high boiling solvent present, part of which appeared as SRC when the distillation cut was made at 482 C.

#### Quality of SRC

The amount of ash and particularly sulfur in the SRC are as important as the yield. If the SRC is to be used as a clean boiler fuel in place of oil, the ash content must be quite low and the sulfur content must be low enough to meet the new source standards for SO<sub>2</sub> emissions during combustion. Average analyses for SRC made from both coals are shown in Table 3. As expected, the average SRC produced in the first step of the two-step process, even using a West Kentucky 9/14 coal blend with an unusually low organic sulfur content (Coal Sample 1) would yield 1.34 lb SO<sub>2</sub>/MM Btu during combustion and would not meet the present new source standards.

There appears to be an increase in the sulfur content of the SRC prepared with 25 weight percent added tetralin in the solvent. Again, this may be due to the absence of a sulfur dilution effect which takes place when low sulfur content solvent appears in the SRC fraction. Adding an overpressure of molecular hydrogen did not affect the sulfur level in the SRC when the second step was carried out at 441 C.

The sulfur in the first West Kentucky 9/14 coal can be divided into organic (1.16 weight percent) and inorganic (2.61 weight percent) fractions. The maximum percentage of organic sulfur removed in the simulated first step was 37 percent (MAF basis) at 454 C, 1 minute residence time, as shown in Figure 3. Sulfur was removed in increasing amounts with increasing reaction time and at increasing rates with increasing reaction temperature. Since there was no effect of increasing solvent to coal ratio on sulfur removal, this suggests that hydrogen was not being transferred from the Wilsonville recycle solvent to the coal molecule in order to remove sulfur at the low temperature used in the first step. The sulfur removal mechanism at this stage probably only involves thermal removal of nonthiophenic sulfur.

#### Other Reaction Products

In addition to SRC, gas, light oil, and a filter cake of unreacted coal and inorganic materials are produced in the first step of the short residence time coal liquefaction process. One of the objectives of short residence time coal liquefaction is to minimize the loss of hydrogen to gases and light oil. Unreacted coal also represents a loss of material, but it may be gasified to produce process hydrogen.

The average quantity and composition of gas from AC1 is shown in Table 3. The  $N_2$ -free gas contained small quantities of  $CO_2$ ,  $H_2S$ , and other gases which resulted from heating coal to 250 C. The average composition and quantity of the  $N_2$ -free gas produced during the reaction in AC2 is also shown in Table 3. Most of this gas is probably also the result of coal decomposition. Only 2 weight percent of the as-fed coal goes to gas during the first step of the process.

TABLE 3. AVERAGE ANALYSIS OF SHORT RESIDENCE TIME COAL LIQUEFACTION PRODUCTS

| <u>Analysis, weight percent<br/>of sample</u> | <u>Product Fraction</u> |                | Light Oil | Filter<br>Cake | Solvent |
|---|-------------------------|----------------|-----------|----------------|---------|
|   | 1st Coal                | 2nd Coal       |           |                |         |
| Moisture                                      | --                      | --             | --        | --             |         |
| Ash   | 0.17                    | 0.15           |           | 48.4           |         |
| Carbon  | 84.3                    | 84.9           | 83.9      | 42.7           | 87.75   |
| Hydrogen                                      | 5.6                     | 5.75           | 7.6       | 2.3            | 7.7     |
| Nitrogen                                      | 1.75                    | 1.7            | 0.7       | 1.0            | 0.73    |
| Sulfur  | 1.02                    | 1.37           | 0.19      | 6.16           | 0.20    |
| Oxygen (by difference)                        | 6.7                     | 6.2            | 7.7       | 3.4            | 3.77    |
| H/C ratio                                     | .797                    | .813           | 1.087     |                | 1.05    |
| <u>Volume Percent of Sample</u>               | <u>Gases</u>            |                |           |                |         |
|   | <u>Preheater</u>        | <u>Reactor</u> |           |                |         |
| $H_2$   | 7.8                     | 11.2           |           |                |         |
| $CO_2$  | 34.8                    | 10.9           |           |                |         |
| $C_2H_4$                                      | 0.55                    | 1.3            |           |                |         |
| $C_2H_6$                                      | 3.5                     | 10.4           |           |                |         |
| $H_2S$  | 29.0                    | 31.3           |           |                |         |
| $CH_4$  | 3.8                     | 23.3           |           |                |         |
| $CO$  | 2.25                    | 4.8            |           |                |         |
| Others, $C_3^+$ , by difference               | 18.83                   | 7.0            |           |                |         |

The  $H_2$  present in the gas in AC2 represents 22 percent of the sulfur in the coal. The total amount of sulfur released into the gas phase during the first step of this coal liquefaction process is 25 percent of the total sulfur in the as-fed coal. This presumably arises from easily removed organic sulfur and some of the pyritic sulfur which can be half converted thermally to  $H_2S$  under the reaction conditions.

Added tetralin, hydrogen overpressure and increased solvent to coal ratios resulted in no measurable increase in gas yield. The results are complicated by and corrected for hydrogen added in the experiments with high-pressure hydrogen.

The average filter cake analysis is also shown in Table 3. Individual filter cake compositions vary widely. As conversion increases, sulfur and ash increase while oxygen and hydrogen and possibly nitrogen concentrations in the filter cakes decrease. The average filter cake yield is 30 weight percent of the as-fed coal. The sulfur present in the filter cake represents 49 percent of the sulfur in the coal feed. This sulfur is made up of the sulfur remaining after partial pyrite decomposition and sulfate sulfur.

#### Solvent Composition and Recovery

The solvent is defined as the product fraction which is soluble in the hot filtrate and/or during the THF extraction of the filter cake and which boils between 232 C and 482 C at atmospheric pressure. One of the requirements of a commercial liquefaction process is that at least as much solvent be created as is used in the process. In addition, the composition of the solvent must be kept constant if it is to be used as a hydrogen donor and as a solvating agent for the dissolved coal.

The average solvent recovery for these experiments in the absence of hydrogen or tetralin was 89 percent, corrected for solvent lost in the residues which remain in the autoclaves and by normalizing mass balances from 95.4 to 100 percent. Of the 11 percent of the solvent unaccounted for directly during the reaction, 5-6 percent is collected in each of the light oil and SRC fractions as discussed earlier. The recovery of solvent, uncorrected for starting solvent which distilled in the light oil and SRC fractions, is shown as a function of reaction time and temperature in Figure 5. There is no correlation with temperature. However, solvent recovery does increase with reaction time and with decreasing solvent to coal ratio.

#### Hydrogen Transfer

The data indicate that there was a net consumption of hydrogen in the presence of high pressure hydrogen. A net production of hydrogen in the absence of high pressure hydrogen is well established. During the liquefaction process, the solvent is presumed to donate hydrogen to the dissolved coal molecules to stabilize them and prevent polymerization reactions which lead to coke. In this study, hydrogen transfer was followed by monitoring the elemental analysis of the solvent to see if a change in hydrogen percentage or H/C ratio occurred. Comparison of the average solvent analyses before and after reaction is complicated by the loss of recovered solvent to SRC and light oil fractions which occurs during distillation.

The analyses for hydrogen and carbon are the same within experimental error, however, if as shown in Tables 2 and 3, hydrogen has decreased 0.1 weight percent and the H/C ratio has decreased 0.02 on the average, this means that approximately 1.3 percent of the hydrogen in the solvent transfers to coal during liquefaction at 3:1 solvent to coal ratio. This indicates that up to 85 percent of the coal can be converted to THF soluble materials by transferring hydrogen amounting to less than 0.3 weight percent of the coal charge. The solvent's role in the first step of the process is clearly based as much on dispersing and dissolving the coal molecules resulting from thermal bond breaking as it is on stabilizing the molecules by hydrogen transfer.

#### Sulfur Balance

The fate of sulfur during the process is also important. The average sulfur balance is shown below.

| <u>Products</u> | <u>Percent of<br/>Sulfur in Coal</u> |
|-----------------|--------------------------------------|
| Gas             | 24.9                                 |
| Light Oil       | 0.4                                  |
| SRC             | 21.2                                 |
| Filter Cake     | 44.4                                 |
| Solvent         | <u>90.9</u>                          |

About one-quarter of the sulfur in the coal remained in the SRC, one-quarter appeared as  $H_2S$  in the gases and nearly one-half remained in the filter cake. Hydrogen introduced in the second step would not see three-quarters of the sulfur contained in the starting coal.

#### CONCLUSIONS

In step one, conversion of coal to a THF soluble product was rapid. The THF solubles were unstable in the presence of a coal derived solvent, but in the absence of hydrogen. In step two, the addition of molecular hydrogen to the system or of tetralin to the solvent to increase hydrogen transfer to the coal increased the THF soluble conversion but did not lower the sulfur content of the SRC. Higher temperatures were required to remove more sulfur.

SRC yields were greater than 100 percent due to the presence of solvent in the SRC. The average SRC prepared from West Kentucky 9/14 coal blends did not meet new source standards for  $SO_2$  emissions after the first step of the two-step process although all of the inorganic sulfur and an average 12 percent of the organic sulfur was removed.

Hydrogen was produced in the absence of an overpressure of molecular hydrogen and consumed when hydrogen was present in the system. During step one of the two-step process less than 0.3 weight percent hydrogen was transferred from the solvent of the SRC in the absence of hydrogen. The solvent appears to physically stabilize the coal. Solvent recovery from step one was approximately 100 percent when corrected for the amounts of starting solvent which were collected in the light oil and SRC fractions.

#### ACKNOWLEDGMENT

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#### REFERENCES

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2. "Short Residence Time Coal Liquefaction", EPRI AF-780, prepared by Battelle's Columbus Laboratories, June, 1978.

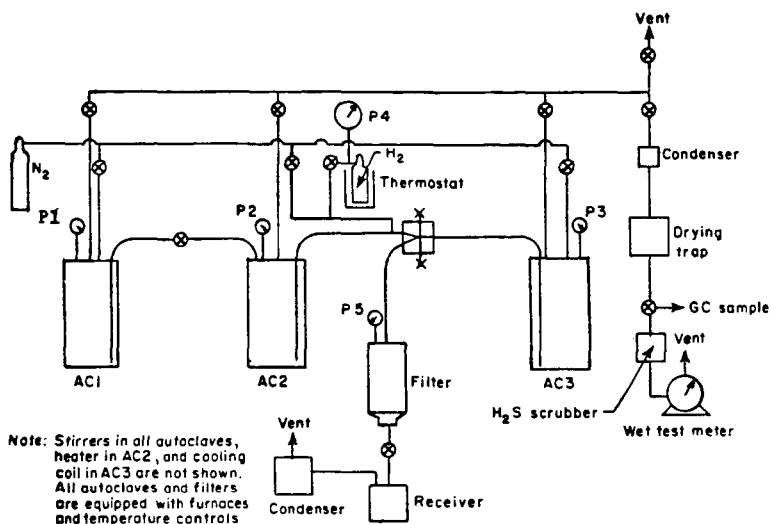


FIGURE 1. SHORT RESIDENCE TIME COAL LIQUEFACTION APPARATUS - 3 AUTOCLAVES

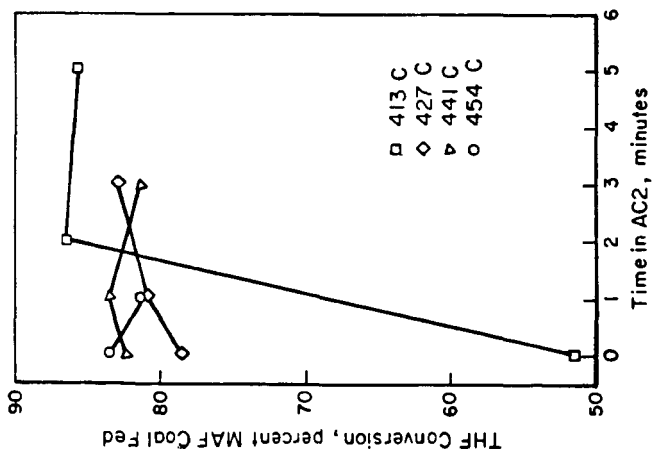


FIGURE 2. THF SOLUBLE CONVERSION VERSUS TIME AND TEMPERATURE

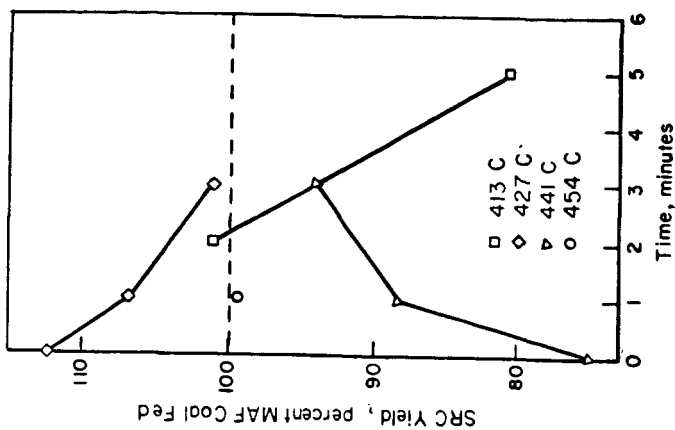


FIGURE 3. SRC YIELD VERSUS TIME AND TEMPERATURE

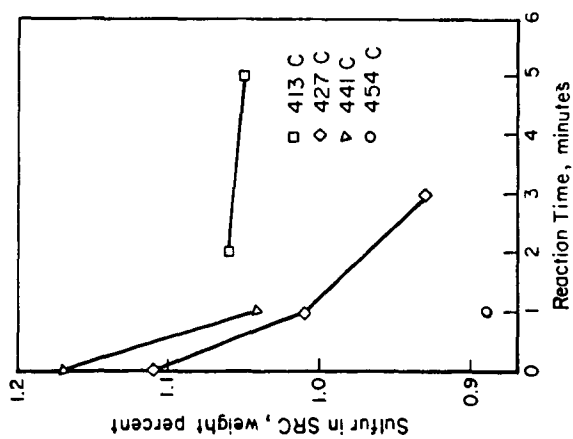


FIGURE 4. SULFUR IN SRC VERSUS TIME AND TEMPERATURE

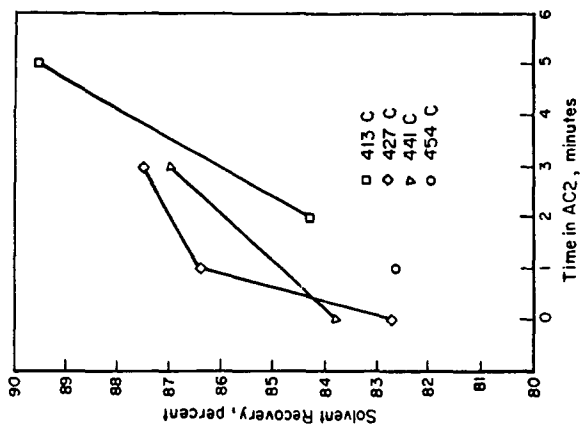


FIGURE 5. SOLVENT RECOVERY VERSUS TIME AND TEMPERATURE